RAW MATERIALS

UDC 666.951:622.362.5

DIATOMITE AND ITS APPLICATIONS

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Translated from *Steklo i Keramika*, No. 2, pp. 18 – 21, February, 2008.

The largest deposits of diatomite in the world and in Russia are presented. The applications of diatomite and the properties of heat-insulating diatomaceous bricks are described.

Diatomites, opokas, tripolis, spongiolites, and radiolarites form a group of sedimentary silica rock consisting predominantly of opal and cristobalite.

The interest shown in the study of silicaceous rock is largely due to their useful properties. These rocks are minerals which possess a wide range of valuable properties. As a result, they are widely used in the national economy. Their characteristic features are the presence of amorphous active silicon dioxide on the one hand and a fine-porous structure, lightness, and low thermal conductivity on the other. These properties make these materials chemically highly active and make it possible to use them as sorbents, desiccants, catalysts, filtering and heat-insulating materials, and catalyst and filler carriers.

Diatomites are light fine-porous rocks consisting mainly of extremely small opaline skeletons (or their fragments) of diatomic algae — diatoms. Diatomites are white, yellowish gray, light gray, and sometimes dark gray, and brownish gray. The dark and brown color of diatomites is due to the presence of organic impurities in them, including plant residues. The pores and the walls of pores of diatoms are often of nanosize, which justifies classifying them as nanomaterials. It is evident on photomicrographs (see Fig. 1) that each skeleton of diatoms in diatomite possesses a clearly ordered micro- and nanoporous structure [1]. This structure and the ordered size distribution of the pores give diatomite a low density and its high, compared with other similar materials, heat-insulating properties, on account of which they are used for thermal insulation of surfaces with temperature 900 – 1000°C.

The number of whole skeletons and their large fragments fluctuates over a wide range in diatomites: from less than 1 μm to more than 1 mm in diameter, the usual size being 10 – 200 μm. The volume mass in a fragment, as a rule, does not exceed 1 and for the best varieties it equals 500 – 700 and even 250 – 300 kg/m^3 (Dzhradzorskoe and Masel'skoe deposits). The true density varies from 2 to 2.66 g/cm^3, i.e., from glassy to the most common crystalline forms (β-quartz) [1].

The character of the bedding and quality of diatomites are strongly associated with the conditions under which they were formed. The largest deposits of diatomites are found in marine sediments.

Diatomites of marine origin, whose source of silica were products of erosion of the surrounding dry land, are most characteristic for epicontinental basins of the Paleogene. The main deposits of diatomites in the countries of the Commonwealth of Independent States have been found in deposits in Povolozh'e (Inzenskoe, Sengileevskoe, Atemarskoe, and others), Transurals, and Western Kazakhstan (Irbitskoe, Kamyshlovskoe, Potaninskoe, Kirgizskoe). Diatomites form beds in the form of layers up to 80 – 100 m thick and large lenses in sandy and sand-opoka formations. Deposits of diatomites of this type are characterized by large reserves and relatively high quality. Comparatively small deposits of

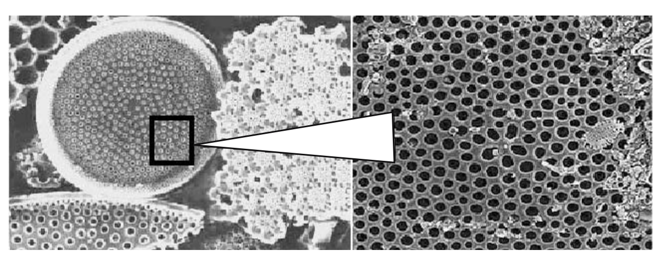

Fig. 1. Skeletons of diatoms and their structure [1].

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diatomites of lower quality are found in Ukraine and in the adjoining regions of Donbass. Abroad, diatomites of this type are encountered mainly in Eastern Europe and for the time being they are not used much.

Deposits of diatomites of marine origin whose silica source were predominately products of volcanic activity are associated with the deposits of piedmont troughs and geosyncline zones. Silica rocks are known in the Okibov zone of the Eastern Carpathians, in the western Pre-Caucasus (Taman Peninsula), on the western shore of Crimea, on Sakhalin, Chaska, Kuril, and Komandor Islands. Commercial deposits have been found in Krasnodar Krai, on the Taman and Kerch Peninsulas, and on Sakhalin. Diatomites of this type (for the territory of the Commonwealth of Independent States) are usually characterized by smaller, than for platform diatomites, productive deposits and in a number of cases contamination with clay and pyroplastic materials, the presence of internal layers of tuffs, tuffites, and so on.

Abroad, the largest deposits of this type in the world are found in Lompoc (USA, state of California).

Diatomites of lacustrine origin, genetically related with the products of chemical erosion of rock on the surrounding land, are most characteristic for regions with a typical glacial landscape. As a rule, they contain aluminum. A large group of commercial deposits of such diatomites has been found in Karelia and, especially, on the Kola Peninsula.

Diatomaceous oozes in large lakes ordinarily fill depressions in basins and accumulate in bays. In shallow lakes they cover the bottom with a continuous layer, and near lake shores diatomite deposits are often seen under a layer of peat. The thickness of diatomite formations rarely exceeds 3 – 5 m, but their quality is very high. The formation of diatomaceous oozes is associated with the postglacial period, and they continue to accumulate at the present time.

Abroad, deposits of diatomites associated with lakes in a glacial landscape are known in Scandinavia, western Scotland, Ireland, Iceland, on the West German plain, in Canada, and on the Atlantic coast of the USA.

Diatomites of lacustrine origin, associated with volcanicogenic – sedimentary formations, are known in the Far East, Trans-Caucusus, and Trans-Carpathia. Large commercial deposits have been found in Primor’e (Pioneskoe), Priamur’e (Chernoyarskoe), Georgia (Kisatibskoe), and Armenia (Dzhradzorskoe, Parbiiskoe, and others). Diatomites are ordinarily bedded in the form of lenses of different thickness in volcanogenic formations (basaltic lavas, tuffs, tuffites, and others). Their deposits are substantially smaller than deposits of diatomites of marine origin, but some of them have very high quality and are among the best on the territory of the Commonwealth of Independent States (Dzhradzorskoe, Kisatibskoe, Parbiickoe).

Large deposits of this type are known in the USA (Nevada, northern Oregon) and in France, Nigeria, on the island of Sicily in Italy, Columbia, Eastern Australia, Japan, Slovakia, Romania, and elsewhere [1].

TABLE 1.

Products	Production of diatomite products, %	
	USA	Russia
Filtering materials	68	< 1
Sorbents	14	< 1
Fillers	12	< 1
Thermal insulation	3	96
Other	3	< 1

Diatomite is used in its natural state and in the form of various fire articles. Ground diatomite is used to fill covers, furnace domes, pipe insulation, for insulating walls, and so forth. The thermal conductivity of diatomite is 0.05 – 0.10 W/(m · K). The volume mass usually equals 200 – 350 kg/m^3 for pure diatomites and reaches 600 kg/m^3 for contaminated diatomites. Diatomaceous powder with up to 15 – 30% added asbestos is also used for fabricating heat-insulating mastics.

The leading producer of diatomite in the world is the USA (about 40% of all diatomite produced in the world). The main applications of diatomites in the world are as filtering materials and sorbents.

Possessing the largest raw materials base of diatomites, Russia trails the industrially developed countries in the use of diatomites. Russia produces 4% of diatomite in the world, of which 96% is used for the production of heat-insulation materials.

In Russia large deposits of diatomites occur in Ul’yanovsk and Penza Oblasts as well as in the Urals and Siberia. More than 70 deposits of diatomite, of which only nine have been thoroughly studied so far, have been found in Ul’yanovsk Oblast. The reserves of diatomites are estimated to be 80×10^6 m^3, which is approximately one fourth of the resources in Russia.

According to data provided by the US Geological Service, the world production of diatomite in 2004 was about 2×10^6 metric tons. The diatomite production volumes by country are as follows (10^3 metric tons): entire world) 1960, USA) 635, China) 370, Russia) 80. The structure of the production of products made from diatomite in the USA and Russia is given in Table 1 [2].

Fire heat-insulation diatomite articles (brick, shells, and segments) are ordinarily manufactured from diatomite with consumable additives (sawdust, shavings, peat). The volume mass can be decreased even more by adding foaming agents. Table 2 gives the characteristics of diatomaceous brick produced domestically and in foreign countries [3].

Heat-insulating diatomaceous brick is used in ferrous and nonferrous metallurgy, power engineering, and glass, cement, and petroleum chemistry industries. It is used for thermal insulation of structures, industrial equipment (electrolyzer reservoirs, melting furnaces, boilers, pipelines, and so

TABLE 2.

Indicator*	Properties of diatomaceous brick, at density (kg/m^3), no more than						
	Domestic producer (“Diatomitovyi Kombinat” Ltd)		Foreign producer (Scamol Company, Denmark)				
	400	500	550	650	750	800	950
Maximum application temperature, °C	950	950	900	900	900	950	1000
Compression strength, MPa, at least	1.6	2.5	1.4	2.5	7.0	10.0	18.0
Thermal conductivity, W/(m · K), no more than, at temperature, °C:							
200	0.096	0.100	0.09	0.13	0.13	0.18	0.24
400	0.097	0.113	0.10	0.15	0.14	0.19	0.27
600	0.117	0.147	0.11	0.17	0.15	0.20	0.29

* The linear temperature shrinkage did not exceed 1% in all cases.

on) with insulated-surface temperatures up to 950°C. In aluminum production it is used for heat insulation of electrolyzers when extracting primary aluminum [4]. Diatomaceous heat insulation is used for fire protection of steel, reinforced concrete, and wooden structures and for effective energy conservation in home construction and civil engineering.

In connection with the increase in the cost of energy carriers, it is becoming necessary to increase the operating temperature of heat-insulation products based on diatomite while preserving its unique properties.

Construction grade diatomaceous brick, fired without consumable additives, is being increasingly used in construction. Such brick is two times lighter than ordinary brick, it is convenient to lay and process, it has high sound-insulation characteristics, and its thermal conductivity is at least as good as that of wood. The thermal insulation properties of such brick largely depend on the volume mass of the initial material and the amount of the clay component. Diatomite is also used in the construction industry as filler for heat-insulating concretes.

Abroad, diatomites have found wide application as sorbents in the petroleum, food, and chemical industries. Diatomaceous powders are excellent filters and they are used in different sectors of the food industry for coarse and fine (clarifying) filtration. They possess high porosity and chemical resistance in acidic media, have no effect on the physical – chemical properties or taste and smell of the filtrate, and permit separating not only mechanical impurities but also colloidal particles.

To obtain high-quality filtering powders it is necessary to use diatomites consisting of predominantly whole skeletons of diatomites with the minimal amount of clay and sand admixtures, as well as organic inclusions and iron oxide. Ordinarily, unprocessed natural diatomaceous powders are of little use as filtering materials. In this connection, the filtering properties of diatomites are improved by calcination up to 1000°C. In this process, organic impurities are removed from the pores, and the volume changes accompanying polymorphic transformations in silicon oxide additionally increase the porosity.

Diatomites are good filters for purifying drinking and industrial waters and can be used successfully in the atomic industry for removing radioactive substances from liquids, primarily the radioactive isotope cesium.

Diatomites and diatomaceous rock are becoming important as carriers of catalysts — they are characterized by high surface area of pores and could retention capacity of the deposited catalyst. They are used together with copper, vanadium, chromium, nickel, and other salts in the oxidation of toluene, anthracene, alcohol, and so forth to accelerate polymerization of hydrocarbons.

In the chemical industry diatomites serve as raw material for obtaining liquid glass. The high dispersity and porosity of diatomaceous particles promote interaction with sodium oxide or hydroxide. Diatomites are natural active mineral additives in portland cement. Their effect as active mineral additives is based on the capability of the amorphous silica present in them to bind lime in low-basicity calcium hydrosilicates according to the following scheme:

$$SiO_2 + Ca(OH)_2 + n(H_2O) = (B)\,CaO \cdot SiO_2 \cdot H_2O.$$

The results of comparative tests of activated diatomites and activated mineral additives of different origin show their effectiveness in construction mixtures for obtaining compositions with high strength characteristics, low shrinkage deformation, high resistance to cold, and resistance to various types of corrosion [5].

In the lacquer and paint industry, diatomites serve as filler which increases the strength of film, viscosity and fire resistance of paints, and resistance of films to rubbing. They facilitate the application of paint with a brush, and they produce films with a mat finish.

Diatomites are an excellent retaining medium. In connection with their high capacity to absorb liquids, they are

used as unique media — carriers of various substances and preparations.

In summary, diatomite has diverse applications because of its unique pore structure. It is most widely used throughout the world as filtration material, sorbents, and fillers. Diatomite is promising for the preparation of nanocomposites, for example, for filling nanopores with various substances.

In connection with the sharp increase in the price of heat carriers, the use of materials made from diatomite as effective heat insulation is becoming more attractive. The drawback of heat-insulation materials made of diatomite is their low temperature of prolonged service in heating equipment (ordinarily no higher than 950°C). Consequently, work on increasing the temperature of prolonged service of heat insulation materials using diatomite as a raw material is important.

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